A THEORETICAL STUDY OF THE SITE SELECTIVITY OF THE CATIONS IN ZEOLITE A. FOR ANTICIPATION OF CATION SITES AND CATALYTIC ACTIVITY

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A theoretical approach was attempted for the interpretation of the site selectivities of the exchangeable alkali and alkaline earth metal cations in zeolite A. The cation-lattice interaction energies comprising the electrostatic, polarization, dispersion, repulsion and charge transfer energies were calculated for the cation at the six- and eight-membered oxygen ring sites in a simplified model of zeolite A structure. As a result, the site selectivities of the cations were determined as follows: Li^+, Na^+, Ca^{2+} and Sr^{2+} ions prefer the six-membered oxygen ring site, whereas K^+, Cs^+ and Ba^{2+} ions prefer the eight-membered oxygen ring site. These results are in good agreement with those obtained experimentally.

Synthetic zeolite A is a crystalline alumino-silicate well known for its industrial applications as an adsorbent and molecular sieve [1]. The characteristic properties of zeolite A are due to the crystal structure which contains interconnected channels and cavities of uniform sizes. In Na_{12}-A [2], of which the ideal chemical composition is $Na_{12}(AlSiO_4)_{12}$, 12 Na^+ ions are distributed among three kinds of site, *i.e.*, four-, six- and eight-membered oxygen ring sites, and for brevity they are named site III, site I and site II, respectively. The eight sites I in a unit cell are occupied by 8 Na^+ ions and the three sites II are occupied by 3 Na^+ ions. The twelfth Na^+ ion occupies one of the eight sites III. These cations are exchanged easily with various others. The exchangable cations have their own intrinsic site preferences [3, 4], that is to say, the three kinds of sites in Na-A zeolite are occupied in an order, not at random, by the incoming cations. This site selectivity of the cation is of great importance in understanding of physicochemical properties of zeolite A, such as adsorption and catalysis, because the adsorption of reactant molecules is prevented partly or completely when the large cations are presented at sites II. The site selectivity of cations was first suggested on the basis of adsorption experiments BRECK [1] and REES and BERRY [4] and has been partly confirmed by X-ray diffraction studies. However, there is no theoretical information available in the literature on the site selectivities of various exchangable cations. We present here a theoretical interpretation of the site selectivity of cations in zeolite A, which are alkali and alkaline-earth metal ions. This is done by evaluating the cation-zeolite lattice interaction energy at each cation site.

Simplified Structure Model of Zeolite A

The bond lengths and angles chosen are those from a single-crystal X-ray diffraction analysis of dehydrated Na_{12}-A zeolite [2]. The structure adopted is a simplified model with high symmetry, which allows easy calculation of the potential energy: bond length (Si, Al)-O = 1.66 Å, bond angles O-(Si, Al)-O = 109.4°, Si-O-Al = 154.4°.

According to PAULING, the amount of ionic character of the (Si, Al)-O bond can be calculated to be 50% from the electronegativity difference between (Si, Al) and O atoms. This indicates that both ionic and covalent bonding components of the framework of zeolite A must be considered in the calculation of the cation-lattice interaction energy. In the case of a purely ionic crystal, the framework is made up of Si^{4+}, Al^{3+} and O^{2-} ions strongly joined together throughout the crystal by ionic forces. In the case of a purely covalent crystal, the framework is composed of Si^0, Al^- and O^0 atoms strongly joined together by covalent forces.

In both cases, it is assumed that the cation is located at a position where the potential energy is minimum at each site.

Energy Calculation

Coulombic electrostatic energy Φ_E

The electrostatic energy between the cation at a given site and zeolite lattice ions can be calculated for various points in the site from the formula

$$\Phi_E = \sum_i \frac{q_M q_i}{r_{Mi}} \tag{1}$$

where q_M and q_i represent the charge of cation (M) and those of zeolite lattice ions (i): +3.5 for Si and Al, −2.0 for O in ionic structure and −1.0 for Al in the covalent structure, respectively, and r_{Mi} is the distance between the cation and lattice ion.

The potential energy of the cation was calculated in order to find the optimum position on the axis throughout the center of each site [2, 5], and the position which gives the minimum electrostatic potential available for the following energy calculations. The axes I and II and the positions of the cation are shown in Fig. 1.

Polarization energy Φ_P

Polarization energy can be represented by the following expression

$$\Phi_P = \frac{1}{2}\alpha_M \left(\frac{d\Phi_E}{dr}\right)^2 \tag{2}$$

where α_M is the polarizability of cation, $(d\Phi_E/dr)$ is the electrostatic field at the cation position along the axis and is obtained from a large scale plot of Φ_E as a function of axial distance, r.

Dispersion energy Φ_D

Several formulae have been proposed to express the dispersion energy. We shall adopt the formula of Kirkwood and Muller for the inverse sixth term and of Kiselev for the inverse eighth and tenth terms.

$$\Phi_D = \sum_i \frac{A_i}{r_{Mi}^6} + \sum_i \frac{B_i}{r_{Mi}^8} + \sum_i \frac{C_i}{r_{Mi}^{10}} \qquad (3)$$

where A_i, B_i and C_i are the functions of m (the mass of an electron), c (the velocity of light), α (polarizability) and χ (magnetic susceptibility).

Repulsion energy Φ_R

For calculation, we shall adopt the Lennard—Jones form D/r^{12} as follows:

$$\Phi_R = \sum_i \frac{D_{Mi}}{r_{Mi}^{12}} \qquad (4)$$

where D_{Mi} is a constant characteristic of the interacting pair, involving contributions of the electrostatic, polarization and dispersion terms, and this can be calculated on the basis of balancing of attractive and repulsive forces at the cation position.

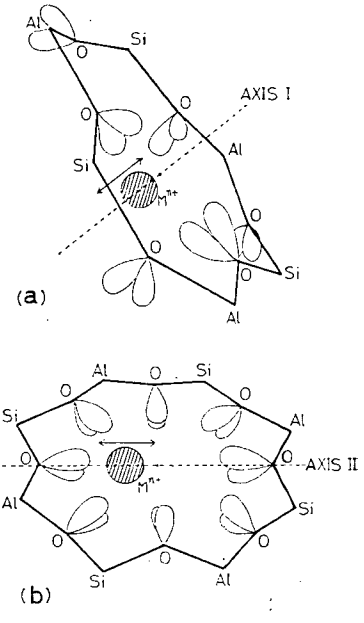

Fig. 1. (a) Site I and symmetry axis I. Unshared-pair orbitals are shown by two lobes on each oxygen. (b) Site II and symmetry axis II. Unshared-pair orbitals are shown by two lobes on each oxygen.

Stabilization energy due to charge transfer Φ_{CT}

The charge transfer in the ionic structure of zeolite A can be left out of the consideration because of instability of the charge transfer structure. This energy is considered only in the case of the covalent structure. If a cation is present near the center of the six- and eight-membered oxygen rings, the unoccupied orbitals on the cation effectively overlap with delocalized unshared-pair orbitals on the ring oxygen atoms, and some degree of transfer of the unshared-pair electron to the unoccupied orbitals may occur. The stabilization energy is produced by this transfer of an electron. The calculation of the energy is carried out based in Mulliken's charge transfer theory [6]. In a system comprising a cation and several oxygen atoms surrounding it at a given site, the energy of the no-bond structure, E_{NB}, consists of the electrostatic energies between charged ions (cation (M^{n+}) and the framework ions), and one-electron energy of a delocalized unshared-pair orbital on the ring oxygen atoms obtained separately. The energy of the system in the charge transfer structure, E_{CT}, consists of the electrostatic energies among the ring oxygen ions donated an electron, $O^{\delta+}$, and Al^- ions in the framework, the cation accepted an electron $M^{(n-1)+}$ and other cations, M^{n+}, and one-electron energy of the unoccupied orbital on the cation. The latter is ap-

proximated by the electron affinity of the cation. The energy of the resonance structure between the no-bond and charge transfer structures, E_{RES}, is obtained by the roots of the following secular determinant:

$$\begin{vmatrix} E_{NB}-E_{RES} & H_{III}-G_{III}\cdot E_{RES} \\ H_{III}-G_{III}\cdot E_{RES} & E_{CT}-E_{RES} \end{vmatrix} = 0$$

where G_{III} is the group overlap integral between the two structures and can result in the overlap integral between the delocalized unshared-pair orbital on the ring oxygen atoms and the unoccupied orbital on the cation, and H_{III} is the resonance integral which is estimated by Helmholz—Wolfsberg approximation. The stabilization energy due to charge transfer, Φ_{CT}, is obtained by the following equation:

$$\Phi_{CT} = E_{RES}-E_{NB} \tag{5}$$

Potential energy of cation in the resonance structure

In ionic and covalent structures, the potential energy of a cation at sites I or II due to the cation-lattice interaction may be expressed as sum of the following terms, respectively:

$$E_{ion} = \Phi_E+\Phi_P+\Phi_D+\Phi_R \tag{6}$$

$$E_{cov} = \Phi_E+\Phi_P+\Phi_D+\Phi_R+\Phi_{CT} \tag{7}$$

The "real" cation-lattice interaction energy in the "real" structure, *i.e.*, the resonance structure between 50% ionic and 50% covalent structures, is obtained as follows:

$$E_{real} = \frac{1}{2}E_{ion}+\frac{1}{2}E_{cov}. \tag{8}$$

Analysis of the Energy Calculation Results

Site selectivity of cations

The E_{real} calculated here by eq. (8) is the result for the first incoming cation into dehydrated zeolite Na_{12}-A by ion exchange. The energy at site III was not calculated since the Na^+ ion at site III seems to be energetically the most unstable of the twelve Na^+ ions. In fact, the potential energy of the Na^+ ion at site III (−5.77 eV) was much smaller compared with those of other sites. Other cations also may not occupy this site from the beginning of ion exchange. The values of E_{real} at sites I and II are summarized in Table I. Most of the E_{real} value is due to Φ_E and other terms such as Φ_P, Φ_D, Φ_R and Φ_{CT} make less contributions to the value. In Table I there is an appreciate difference in the values of E_{real} for sites I and II. It is reasonable to assume that the cation introduced by ion exchange occupies preferentially the site possessing higher potential energy and that it is more stabilized. Thus, from the comparison between sites I and II in E_{real}, the site selectivity of the exchange cation can be determined (the fourth column in Table I).

Table I

Cation-Lattice Interaction Energies in Zeolites A *and Site Selectivities*

Cation	Site	E_{real} eV	Site Selectivity	
			this method	experimental
Li^+	I	−9.46	I	I [7]
	II	−9.13		
Na^+	I	−9.52	I	I [3, 5]
	II	−8.81		
K^+	I	−8.51	II	II [4, 8]
	II	−8.63		
Cs^+	I	−7.85	II	II [9]
	II	−8.83		
Ca^{2+}	I	−24.21	I	I [5, 8]
	II	−22.90		
Sr^{2+}	I	−23.86	I	I [10, 11]
	II	−22.81		
Ba^{2+}	I	−22.30	II	No data available
	II	−22.52		

Comparison with experimental results

As can be seen in Table I, there is good agreement for all cations between the present and experimental results, except for Ba^{2+} ion. It is interesting that Ba^{2+} ion prefers site II, unlike other alkaline-earth metal cations. Unfortunately, there is no information delineating the cation sites and site selectivity of Ba^{2+} ion in dehydrated Ba-A, because the thermal stability of zeolite A is reduced considerably when Ba^{2+} ions introduced into the crystal, and structure collapse occurs on calcination of hydrated (Ba^{ex}, Na)-A. We expect that the site selectivity of Ba^{2+} ion supposed here will be confirmed by a refined X-ray diffraction analysis when a stable dehydrated sample is obtained.

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